

# Analytical Investigation of Fuel Cells by Using In-situ and Ex-situ Diagnostic Methods

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THERMEC'2009 – International Conference on Processing & Manufacturing of Advanced Materials  
Berlin, August 25-29, 2009



# Outline

- Introduction
- Spatially Resolved Measuring Technique for PEFC/DMFC
- Investigation of PEM Fuel Cells With Combined In-situ and Ex-situ Methods
- Spatially Resolved Measuring Technique for SOFC
- Conclusion



## Motivation for Using Diagnostic Tools

- To understand the processes in fuel cells in great detail
  - Influence of the operating conditions on the conditions inside the fuel cell
  - Understanding of degradation processes
  - Inhibition of degradation processes
- To support the development and improvement of fuel cells
  - Detection of problems of components
  - Targeted development
- To control fuel cell systems
  - Optimization of operating conditions
  - Increase of lifetime
  - Early error detection, increased reliability



# Investigation of Degradation Processes

## Physical methods (ex-situ diagnostics)

- Scanning Electron Microscopy (SEM/EDX)
- X-Ray Photoelectron Spectroscopy (XPS)
- X-Ray Diffraction (XRD)
- Porosimetry with mercury intrusion & nitrogen adsorption
- Temperature Programmed Desorption / Reduction / Oxidation (TPD / TPR / TPO)

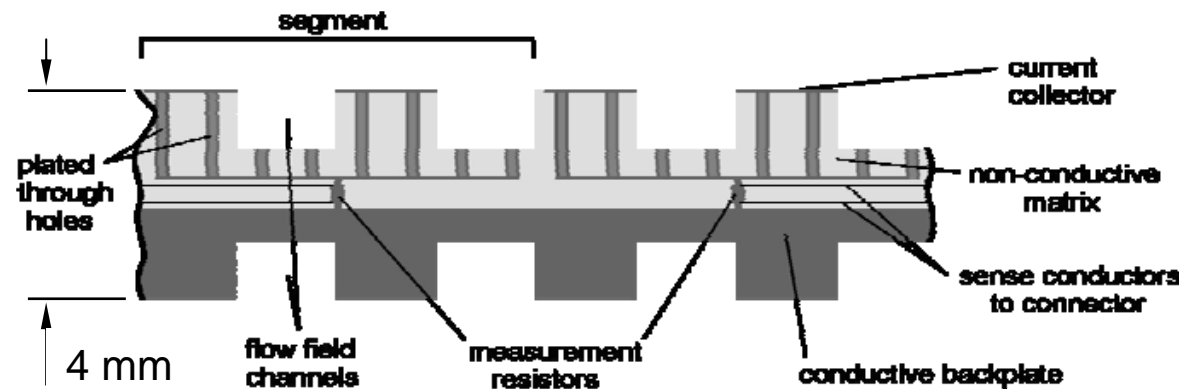
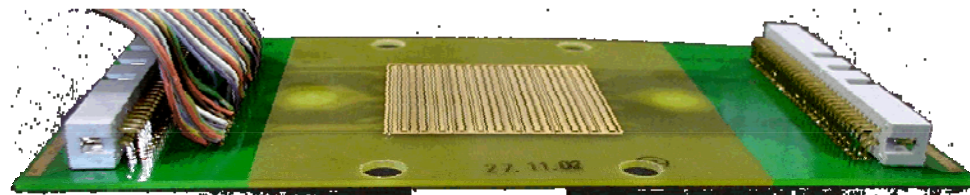
## Electrochemical methods (in-situ diagnostics)

- I-V characteristics
- Electrochemical Impedance Spectroscopy (EIS)
- Locally-resolved measurements (e.g. current density distribution)



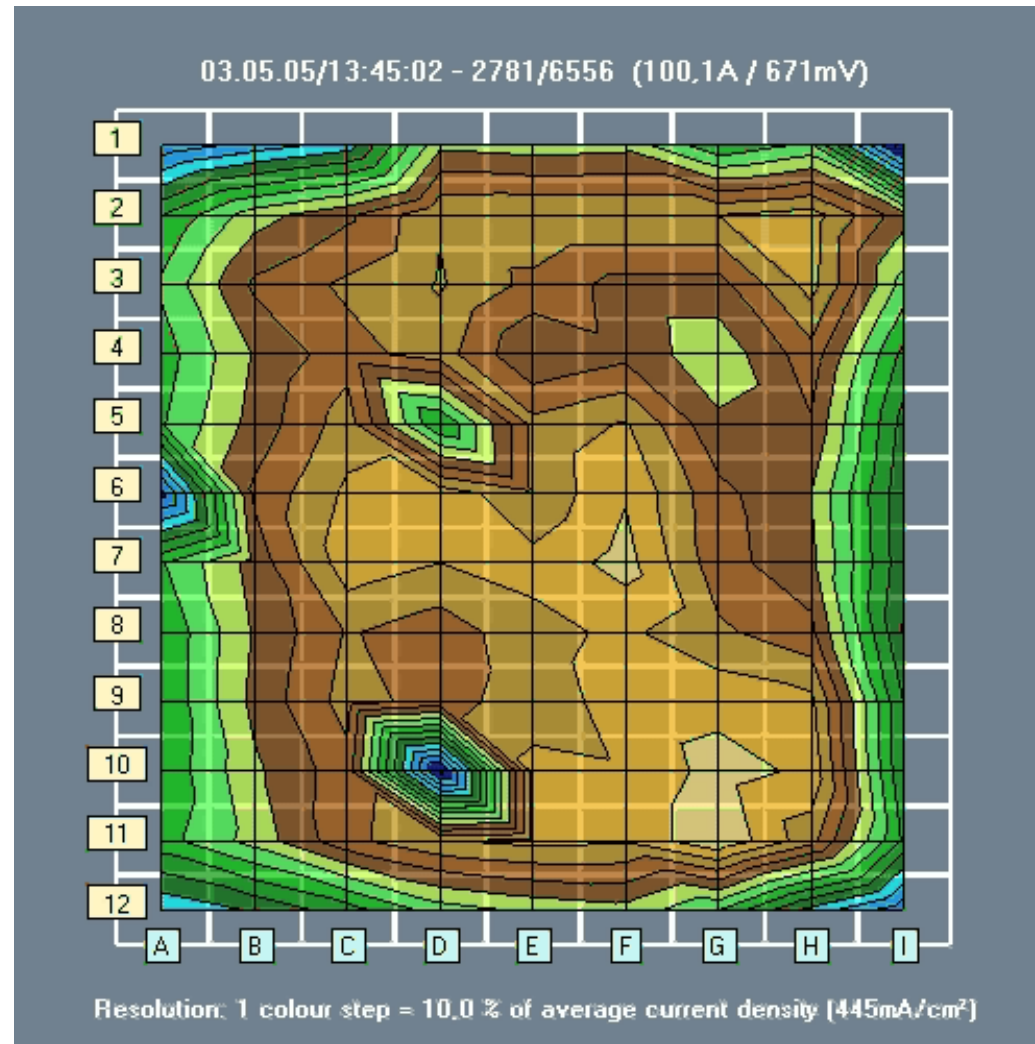
# Segmented Cells for Locally Resolved Diagnostics

Current density, Temperature, Impedance Spectroscopy



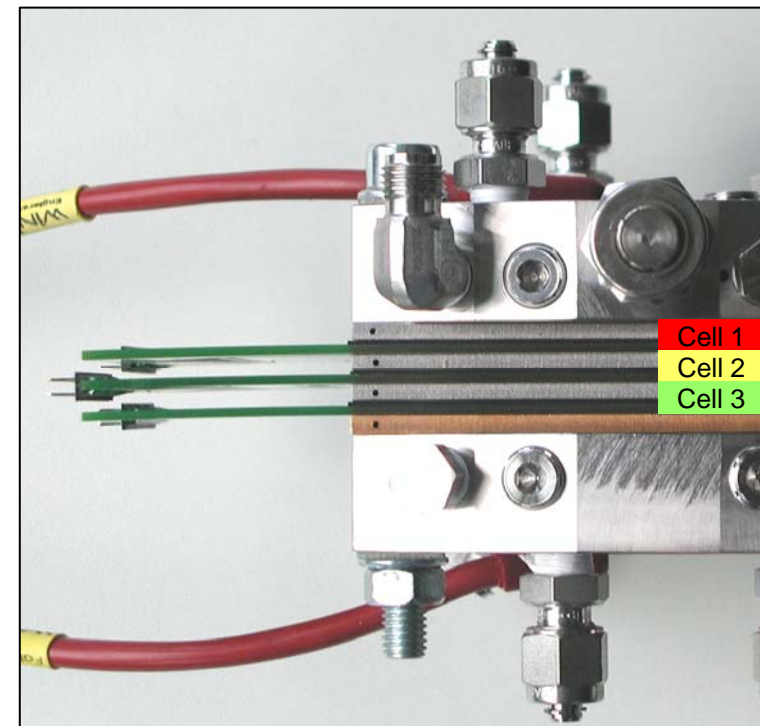
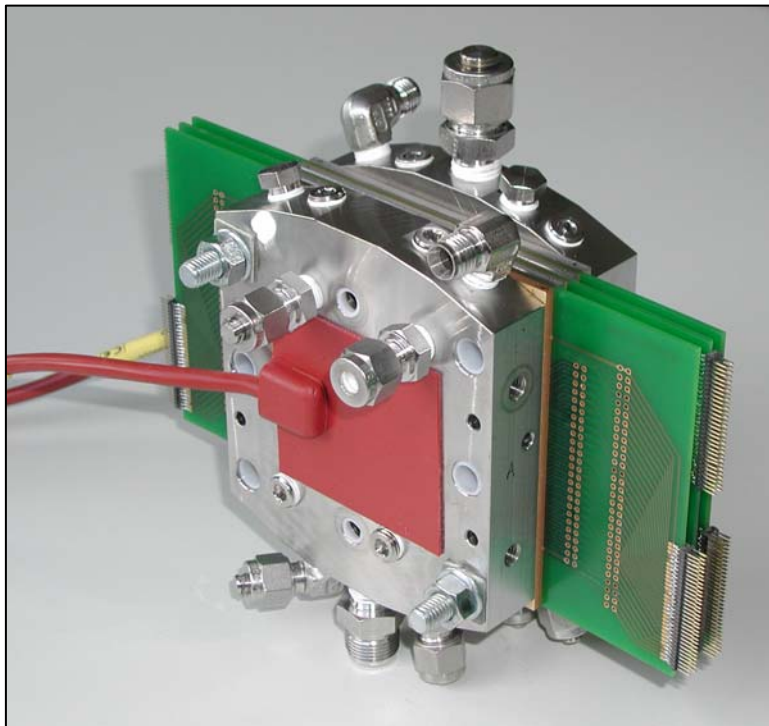


# Current Density Distribution at Reduced Humidification

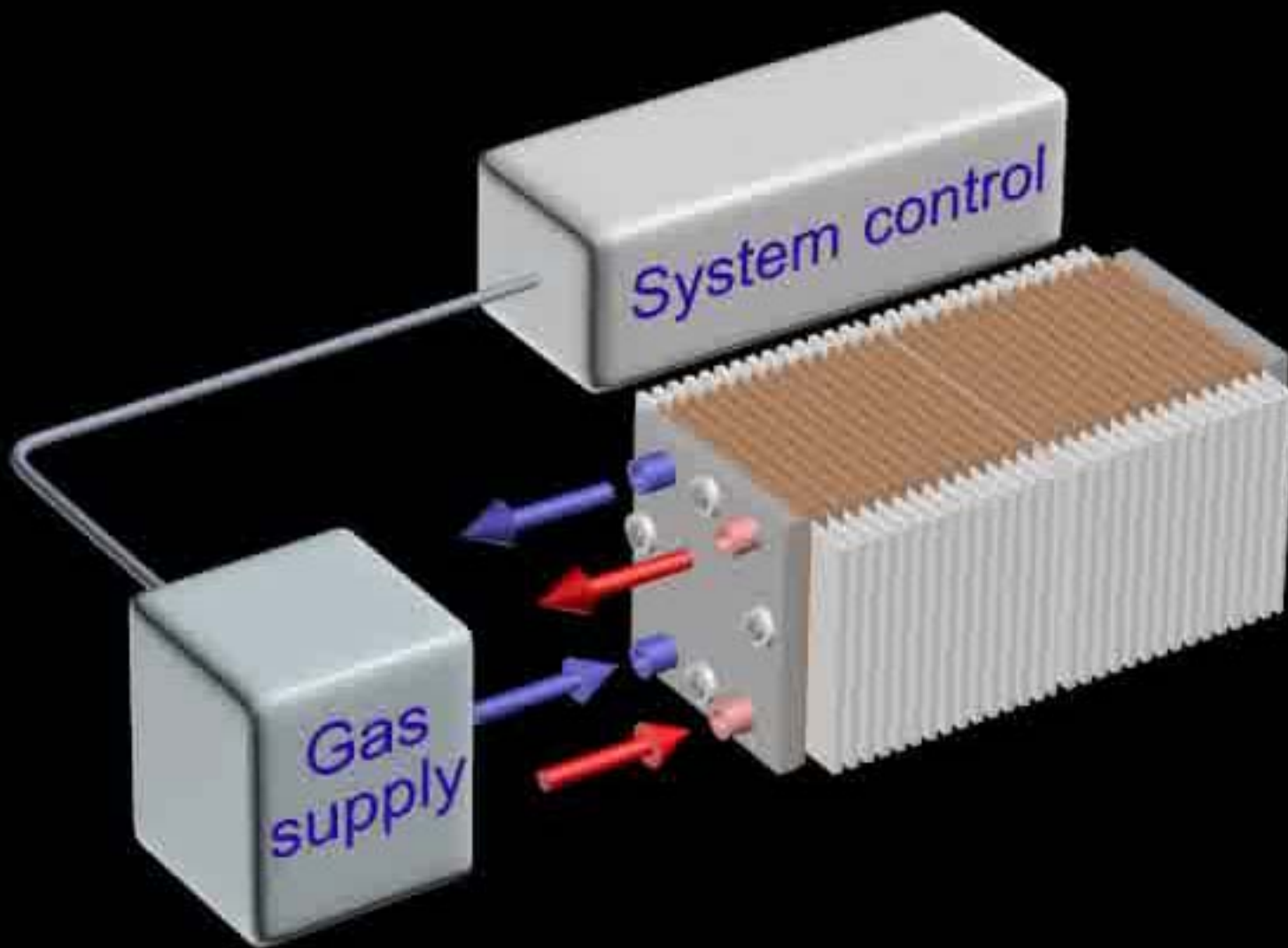




# Integration of Segmented Bipolar Plates in a Shortstack

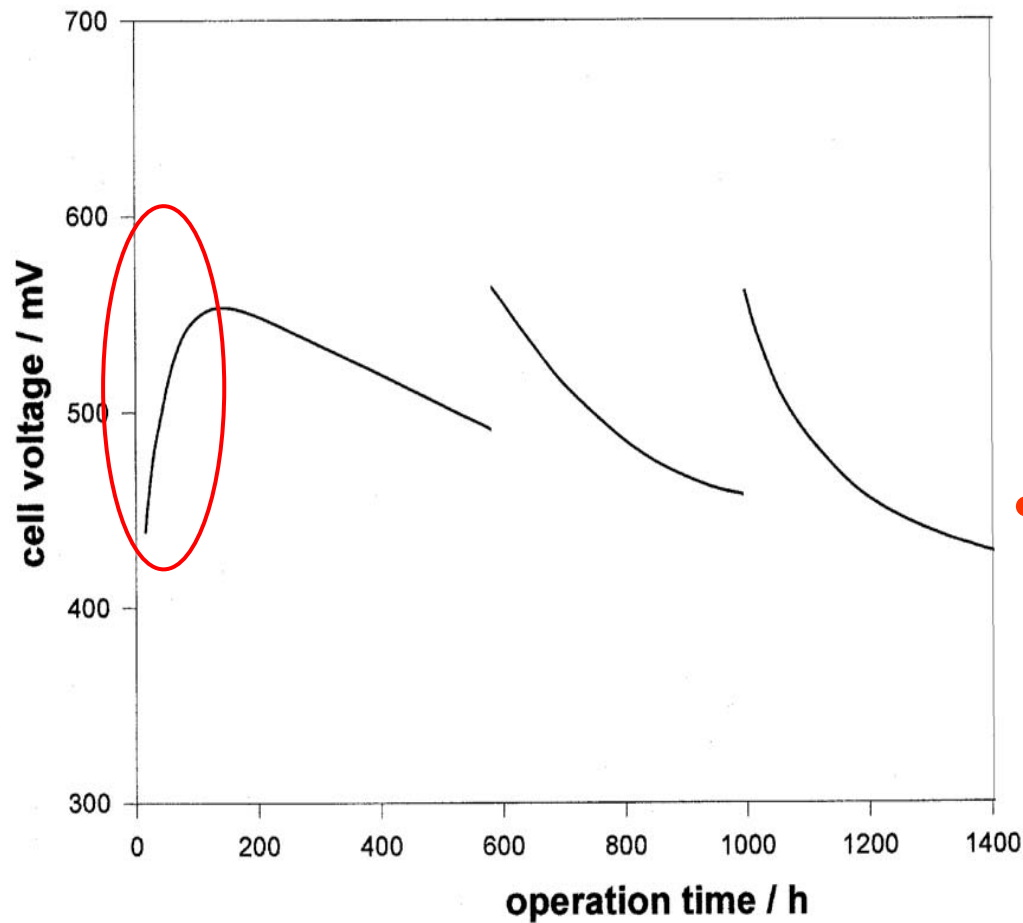


# Sensor - Control System





# PEFC Long-Term Experiment



Nafion 1135

Pt 0.2 mg/cm<sup>2</sup> each electrode

T = 70 °C

p<sub>H2</sub> = 2 bar, dead end

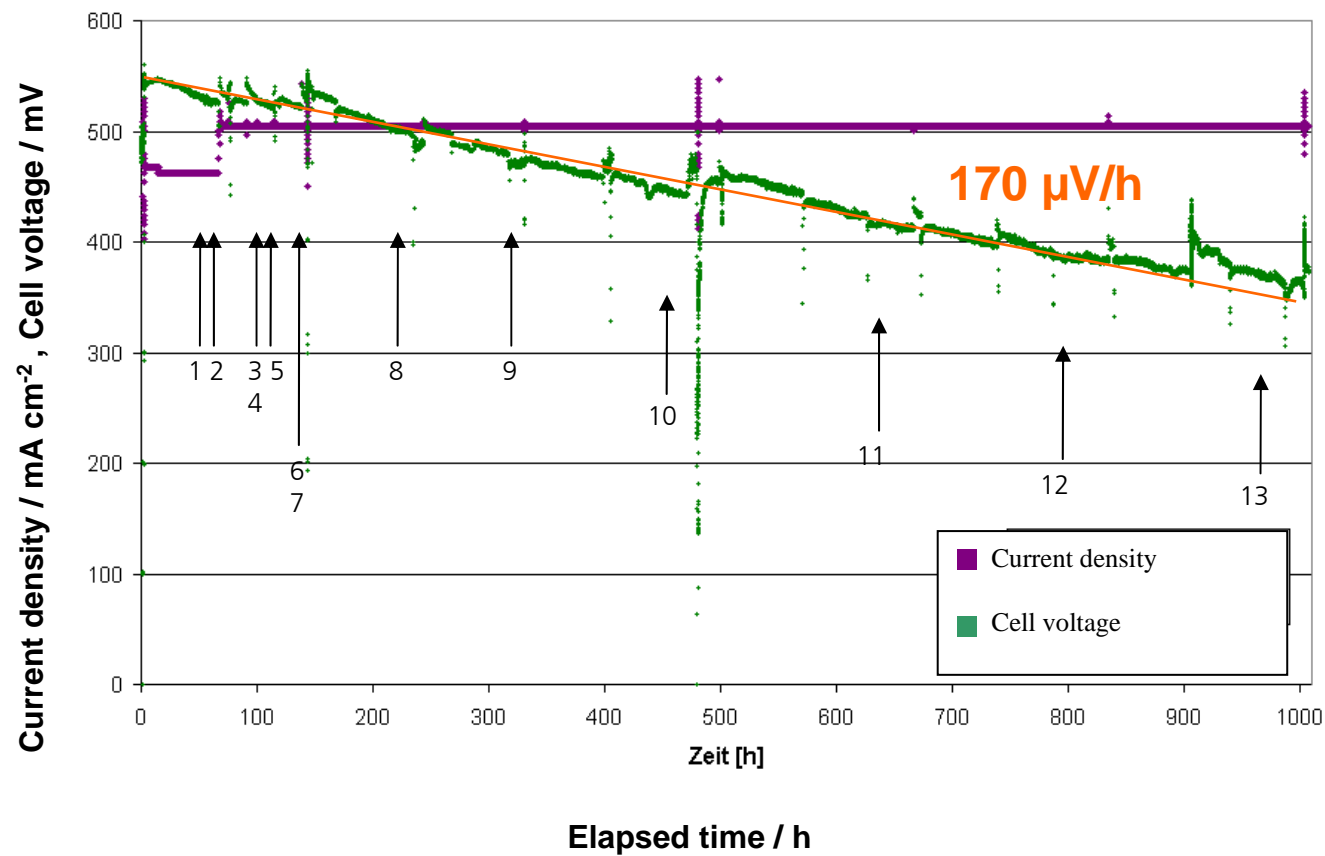
p<sub>air</sub> = 2 bar, λ<sub>air</sub> = 2

i = 300 mA/cm<sup>2</sup>

- The electrochemical performance increases during start-up

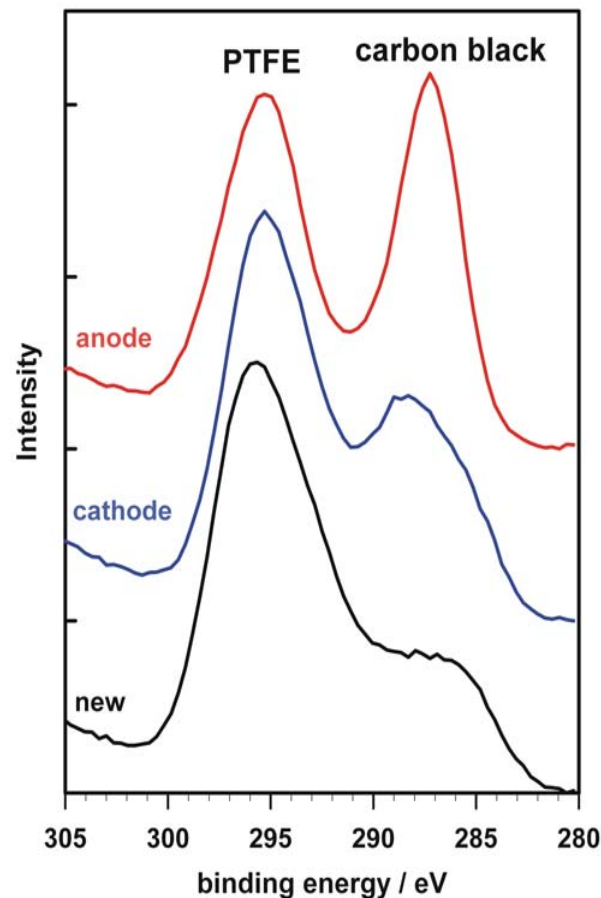


## Change of Cell Voltage During Constant Load at 500 mA cm<sup>-2</sup>



# Degradation in PEFC

## X-ray photoelectron spectroscopy



- Partial decomposition of PTFE identified by X-ray photoelectron spectroscopy
- PTFE decomposition mainly on the anode

→ Decrease of hydrophobicity

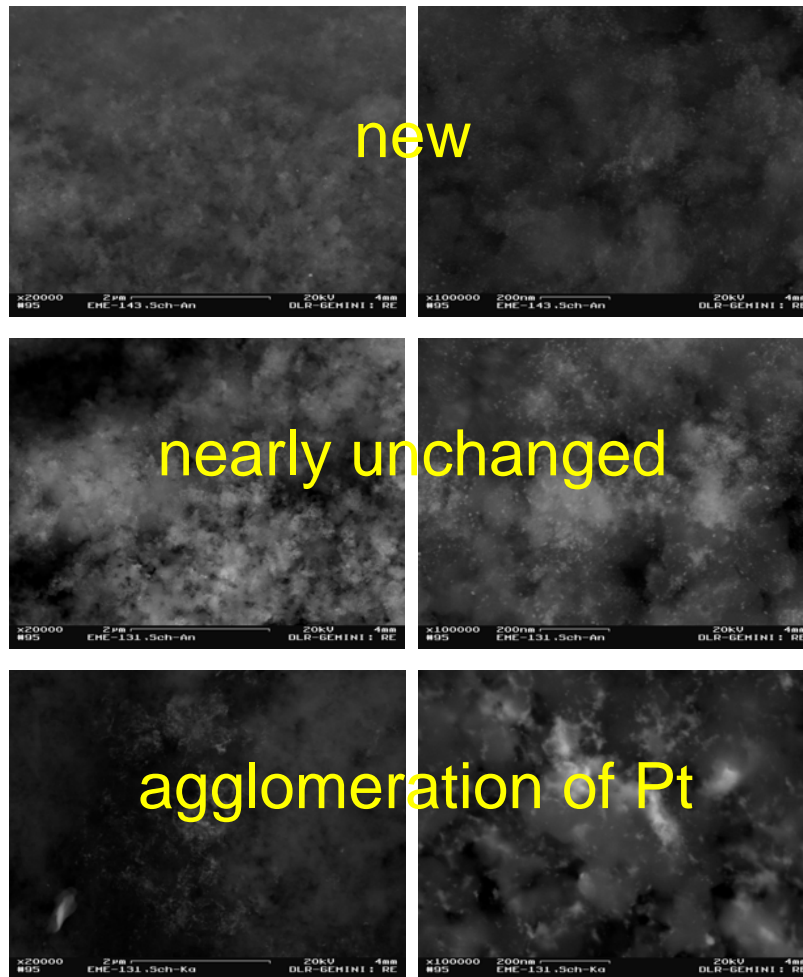
→ Changed water balance

→ Reversible loss of electro-chemical performance



# Investigation of Degradation Processes

## Platinum catalyst



**Reaction layers** in MEAs,  
prepared by the  
DLR dry spraying technique

Top: **new** electrode

Middle: **anode** reaction layer  
of an used MEA, normal  
operation

Bottom: **cathode** reaction layer  
of an used MEA, normal  
operation

Left side:  
**20.000** fold magnification

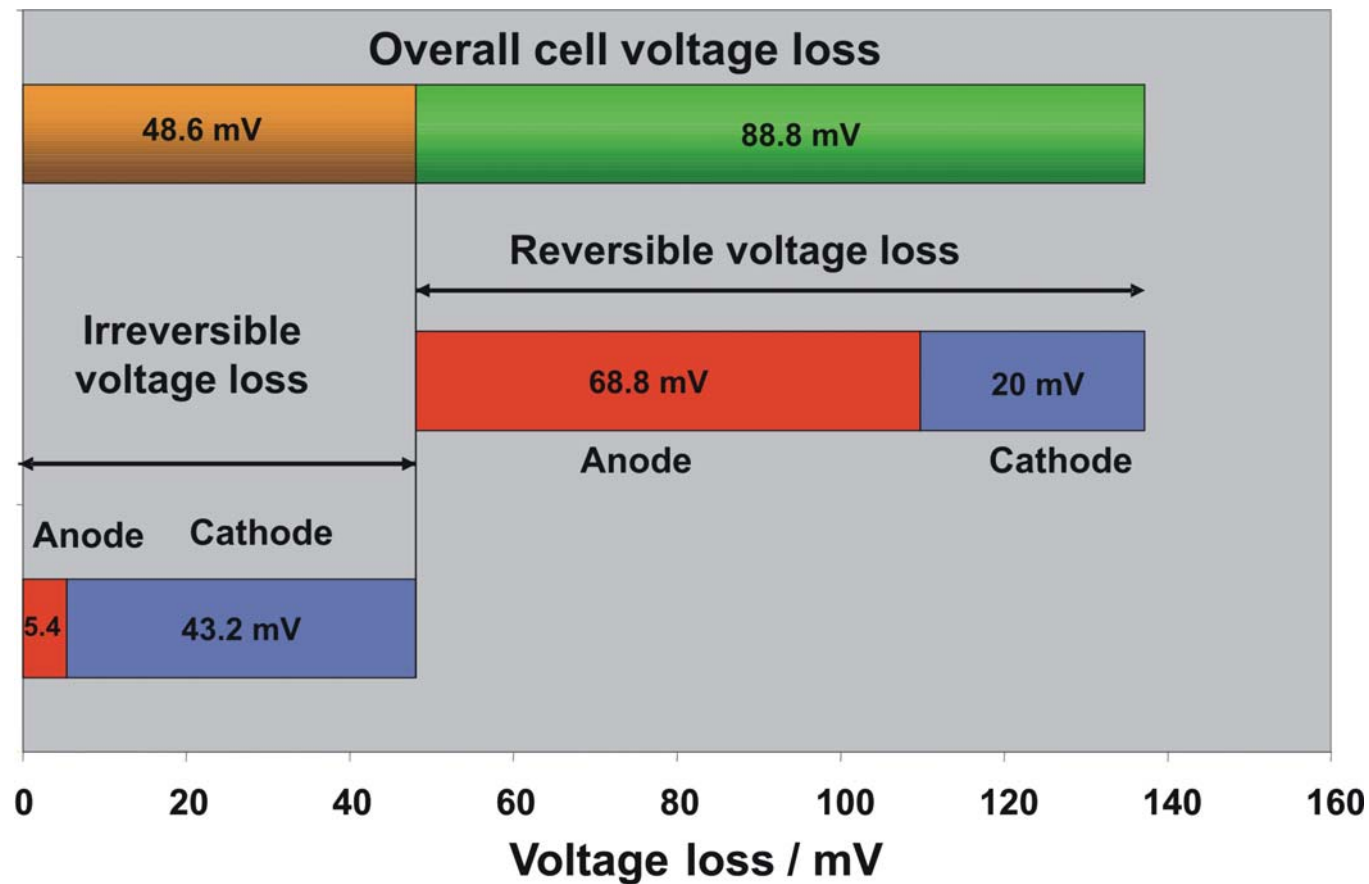
Right side:  
**100.000** fold magnification





# Degradation in PEFC

## Quantification of voltage losses during degradation by EIS



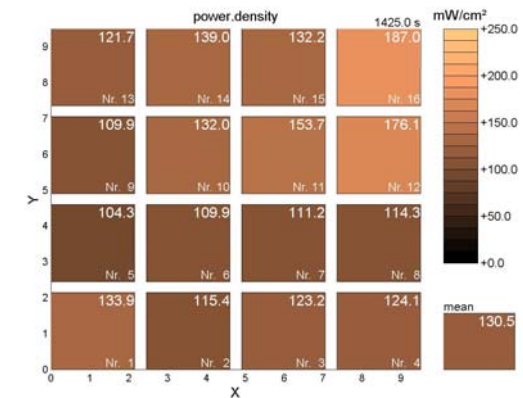
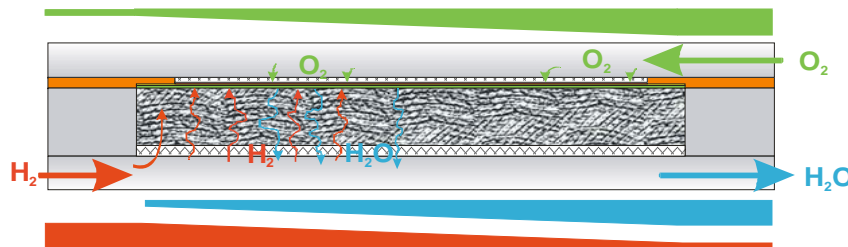




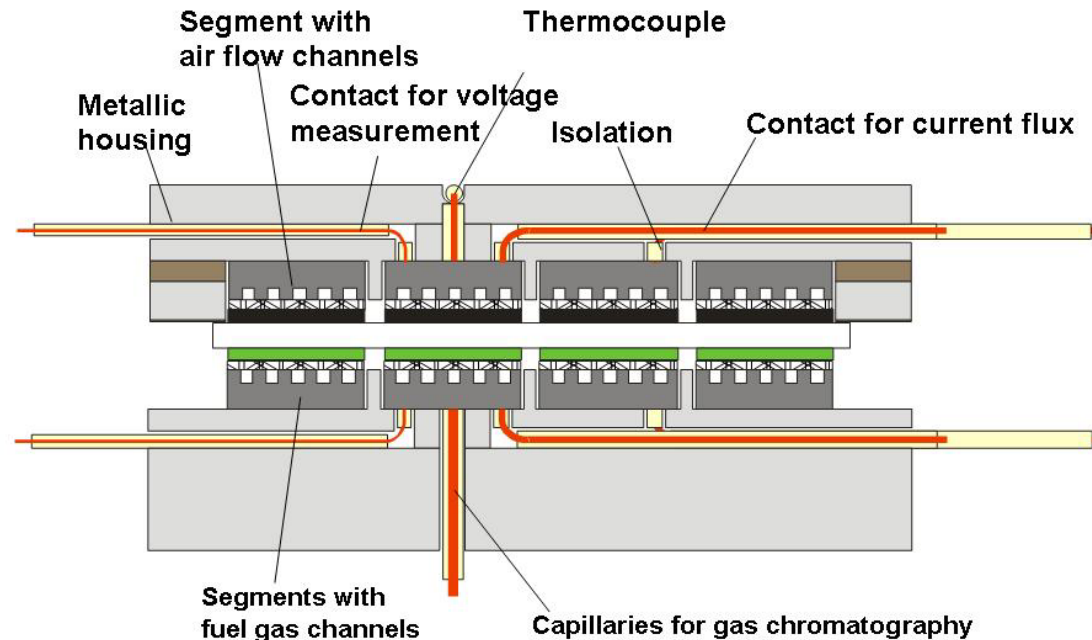
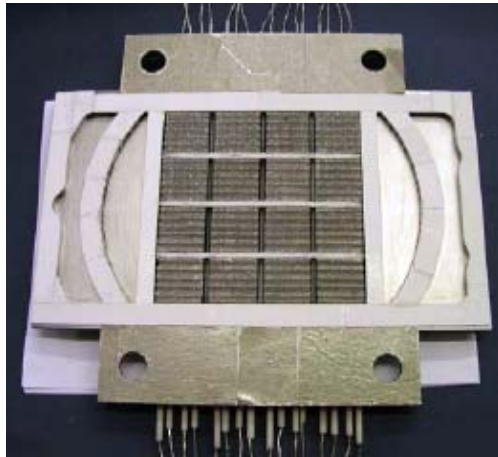
## Motivation

- Strong local variation of gas composition, temperature, current density
- Distribution of electrical and chemical potential dependent on local concentrations of reactants and products

- Reduced efficiency
- Temperature gradients
- Thermo mechanical stress
- Degradation of electrodes



# Measurement Setup for Segmented Cells

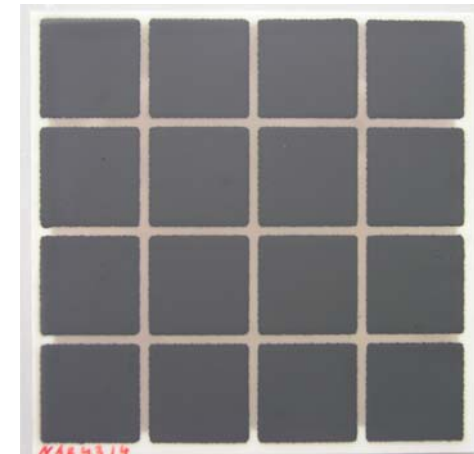


- 16 galvanically isolated segments
- Local and global i-V characteristics
- Local and global impedance measurements
- Local temperature measurements
- Local fuel concentrations
- Flexible design: substrate-, anode-, and electrolyte-supported cells
- Co- and counter-flow



## Segmented Cells

- Anode supported cells with segmented cathode (H.C.Starck/InDEC)

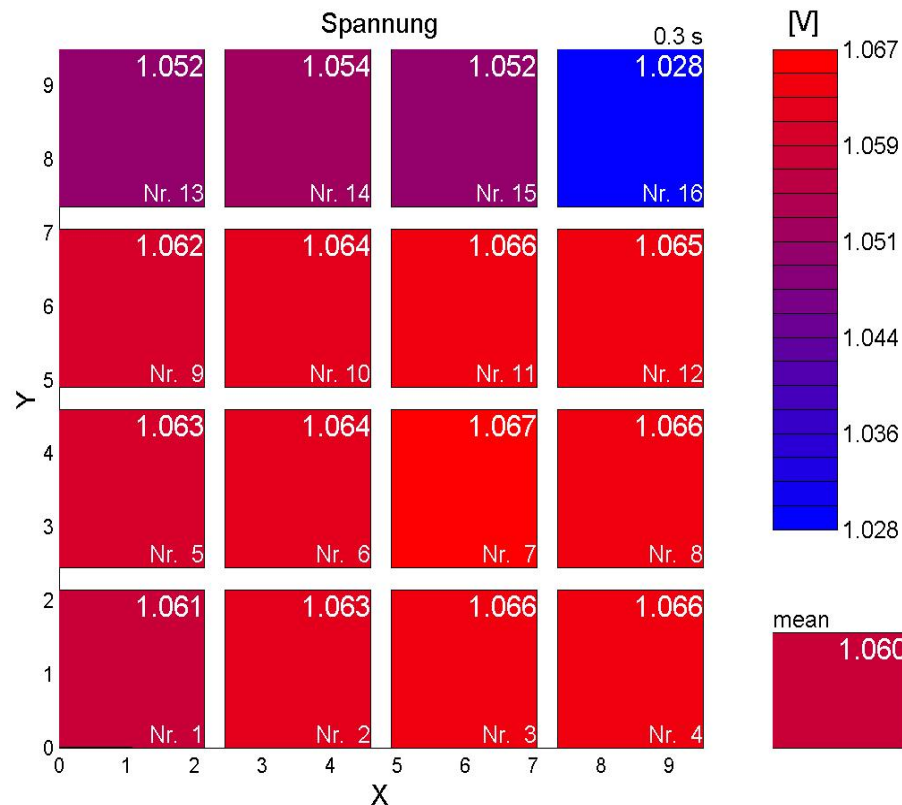
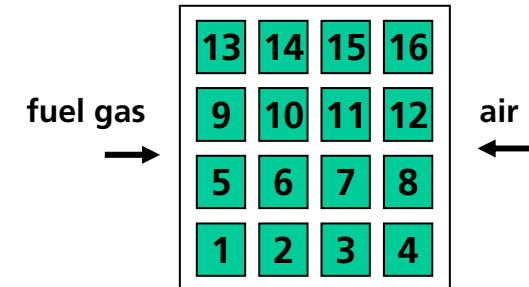


- Electrolyte supported cells: segmented cathode and anode



# OCV Voltage Measurement for Determination of Humidity

- Voltage distribution at standard flow rates:
- 48.5% H<sub>2</sub>, 48.5% N<sub>2</sub> + 3% H<sub>2</sub>O, 0.08 SlpM/cm<sup>2</sup> air



Nernst equation:

$$U_{rev} = U_{rev}^0 - \frac{RT}{zF} \ln \left( \frac{p_{H_2O}}{\sqrt{p_{O_2} p_{H_2}}} \right)$$

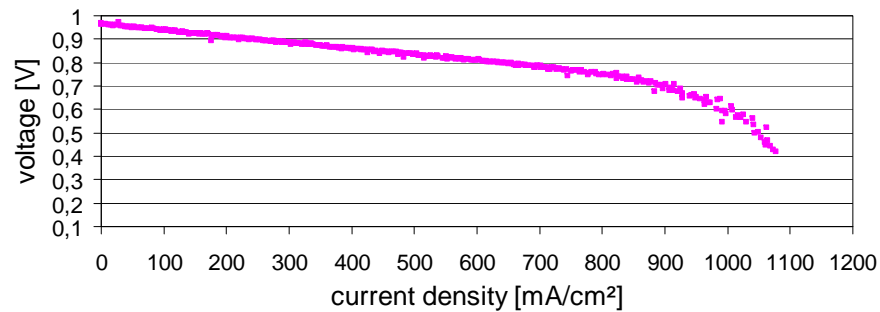
Produced water:

S4: 0.61%, S8: 0.72%,  
S12: 0.78%, S16: 3.30%



# Locally Resolved I-V Characteristics at High Fuel Utilisation

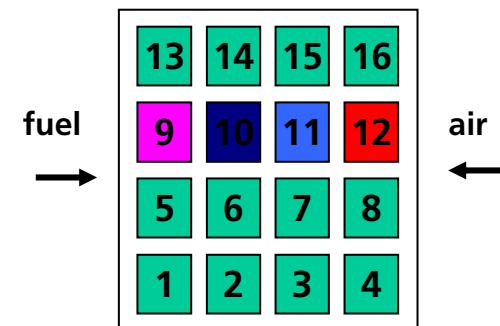
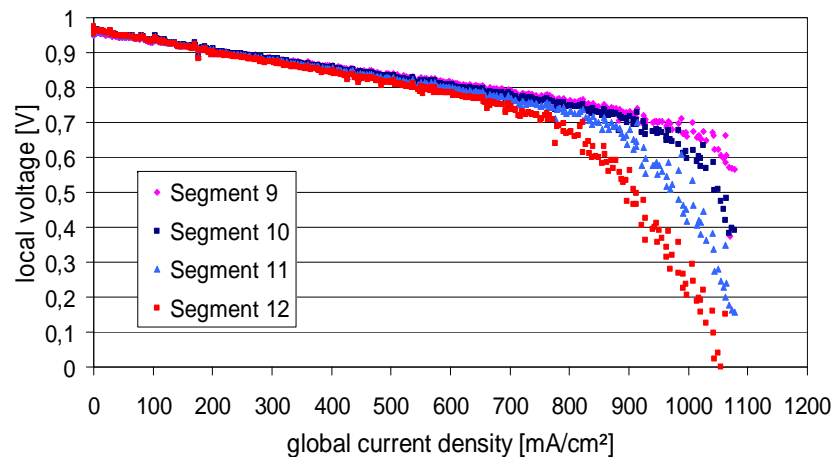
Global I-V characteristics:



50% H<sub>2</sub>, 50% H<sub>2</sub>O;  $fu_{\max} = 60\%$

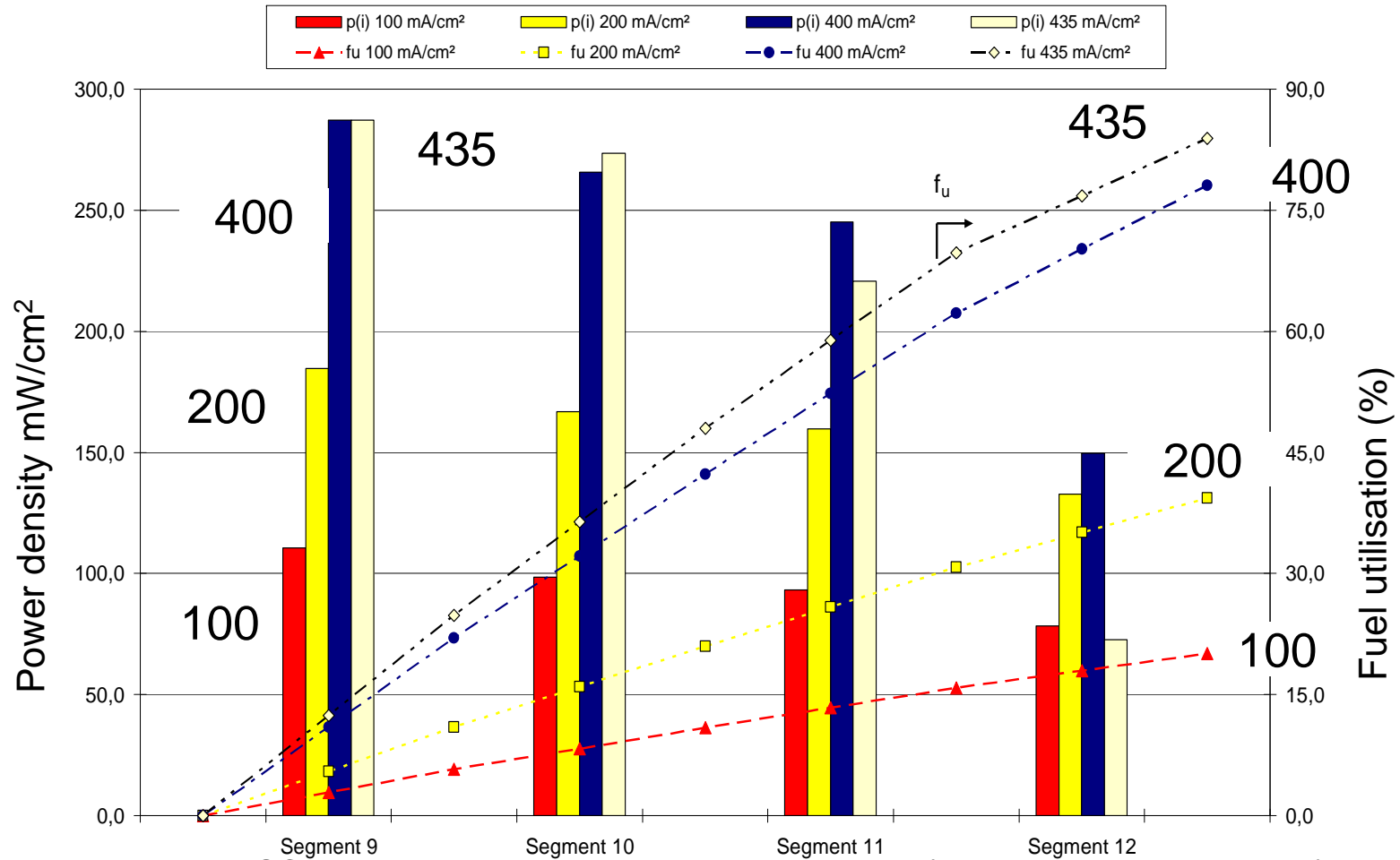
50% O<sub>2</sub>, 50% N<sub>2</sub>

Local I-V characteristics:





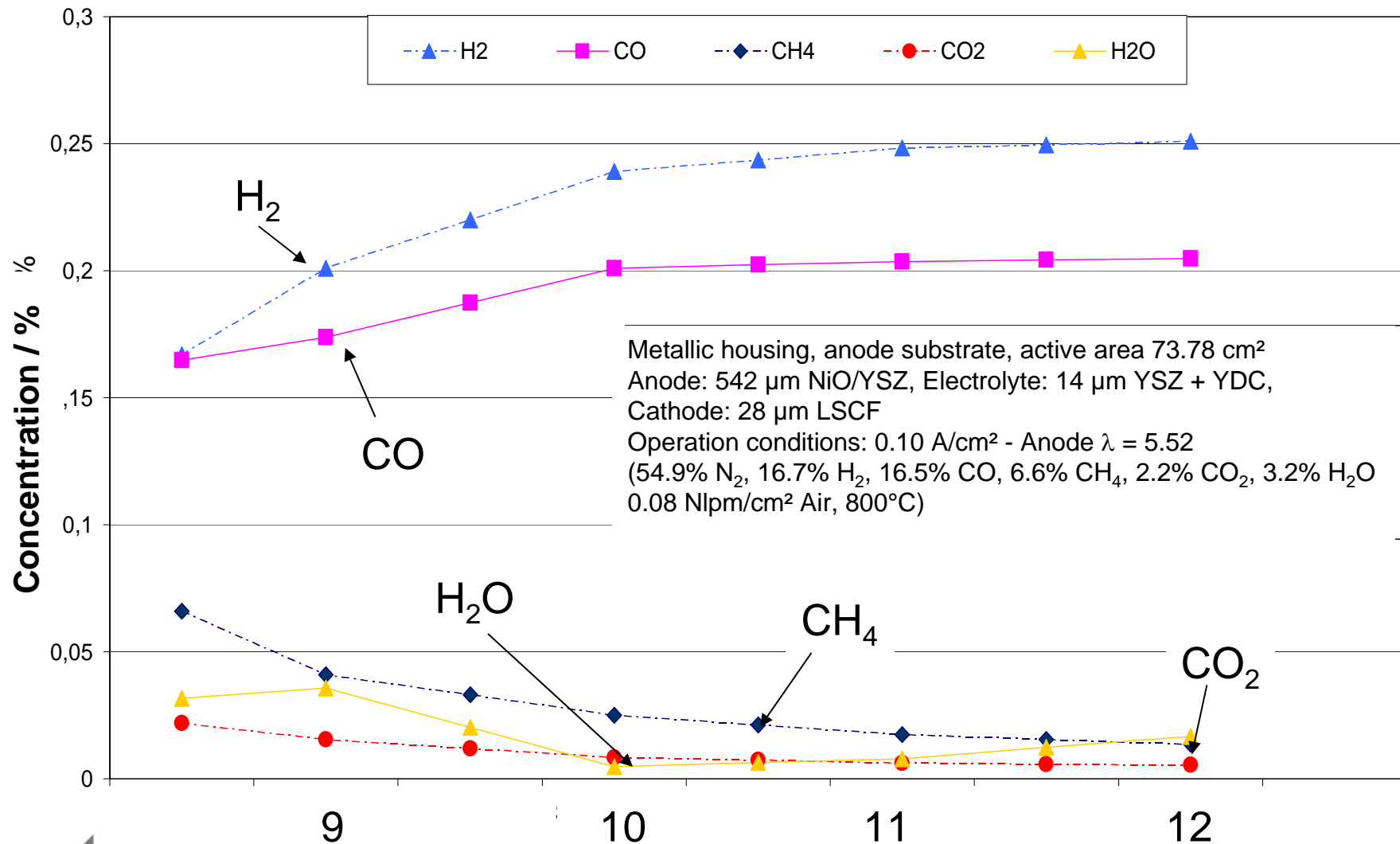
# Variation of Load - Reformate



Anode supported cell, LSCF cathode, 73,96 cm<sup>2</sup>, gas concentrations (current density equivalent): 54.9% N<sub>2</sub>, 16.7% H<sub>2</sub>, 16.5% CO, 6.6% CH<sub>4</sub>, 2.2% CO<sub>2</sub>, 3.2% H<sub>2</sub>O (0.552 A/cm<sup>2</sup>), 0.02 SlpM/cm<sup>2</sup> air

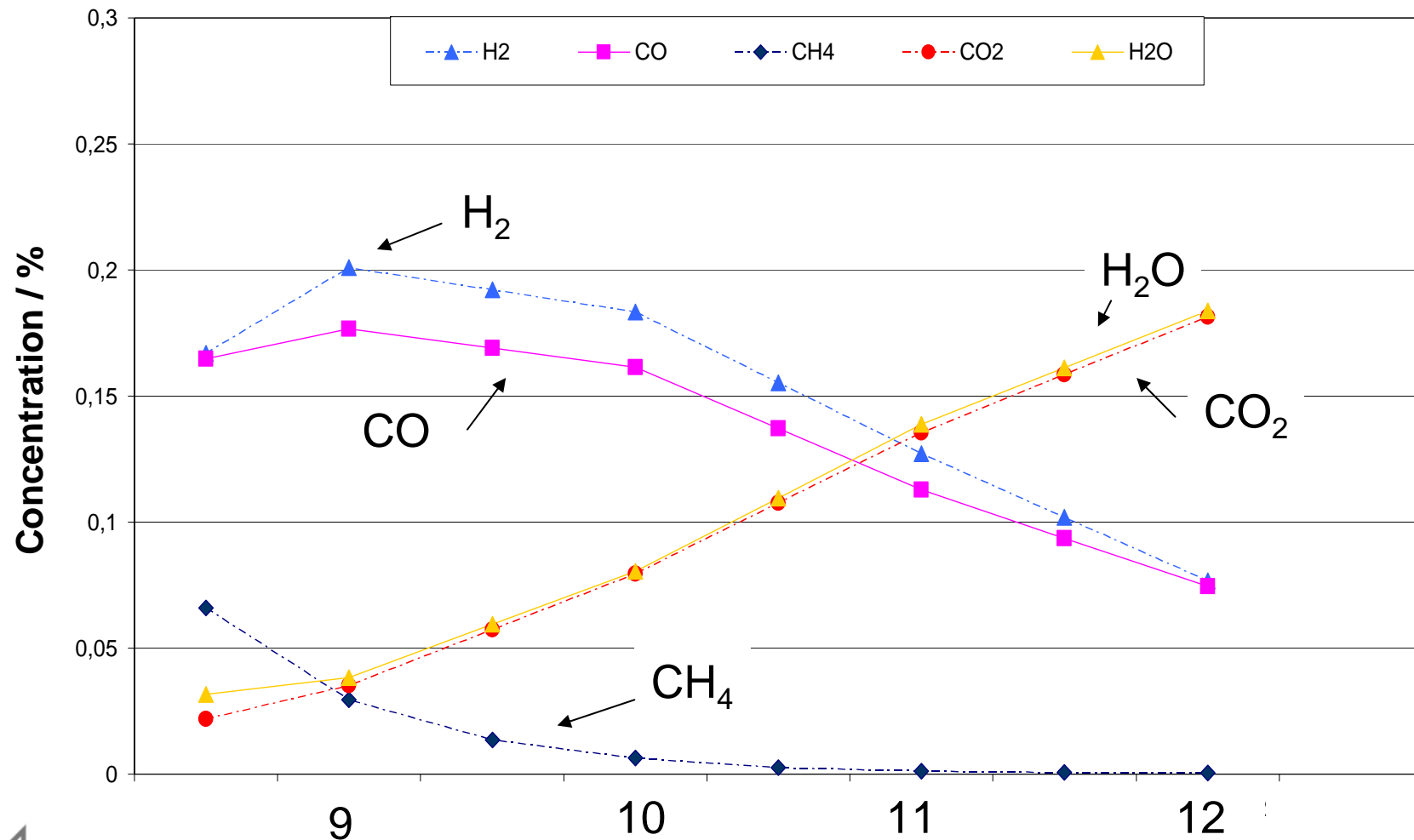


# Reformate: Changes of the Gas Composition at 0 mA/cm<sup>2</sup>





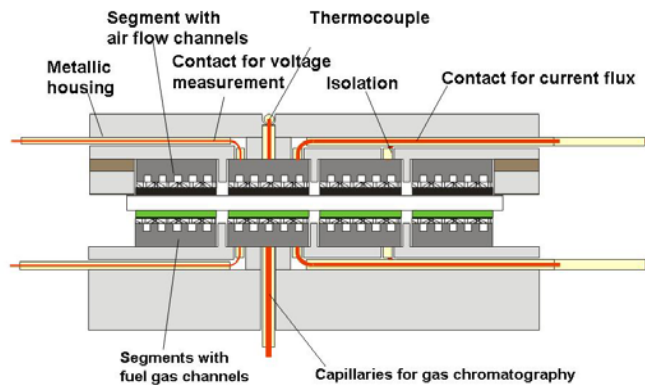
## Alteration of the gas composition at 435 mA/cm<sup>2</sup>



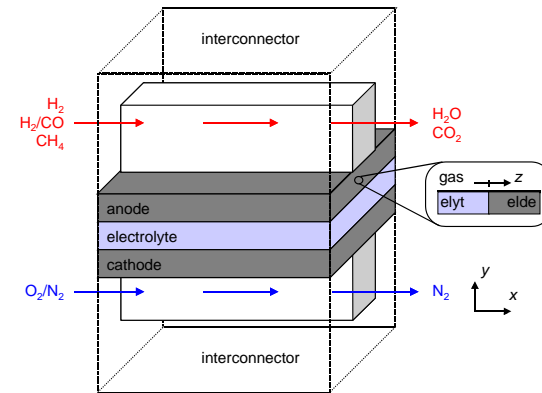
# Combined Experimental and Modeling Approach

Objectives of the study:

- Better understanding of the local variations
  - Identification of critical conditions
  - Optimisation of cell components



Experiments on single segmented SOFC



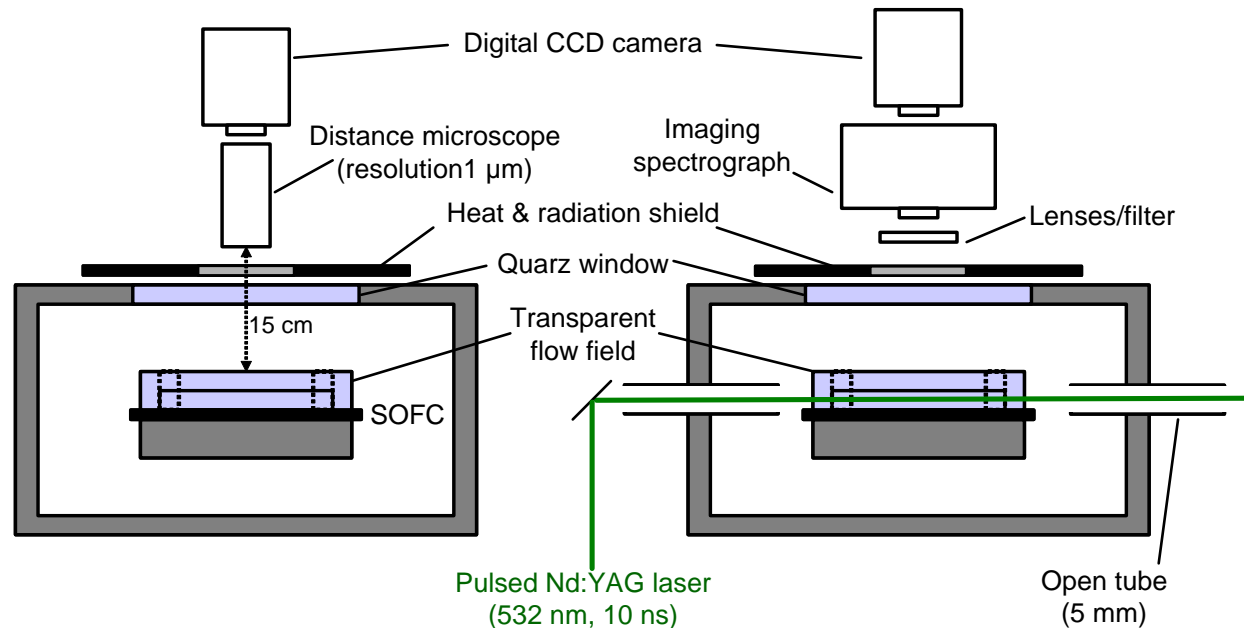
Electrochemical model of local distributions



# Potential for Optical Spectroscopies

a) *In situ* microscopy

b) *In situ* Raman laser diagnostics



- Raman spectroscopy
- Laser Doppler Anemometry (LDA)
- Particle Image Velocimetry (PIV)
- Fast-Fourier Infrared (FTIR)
- Coherent Anti-Stokes Raman Spectroscopy (CARS)
- Electronic Speckle Pattern Interferometry (ESPI)

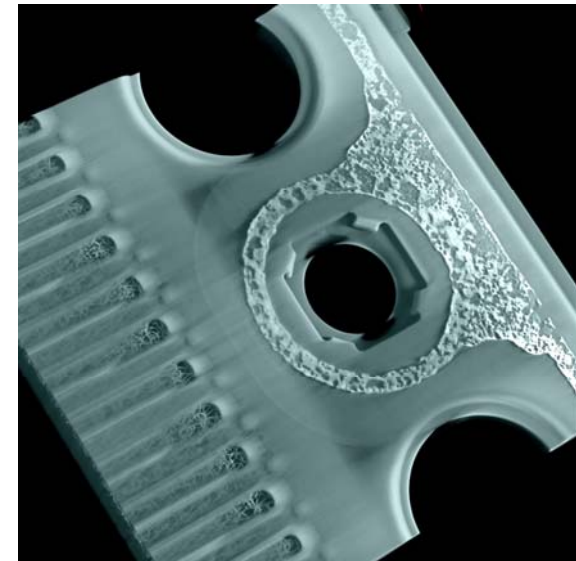


# X-Ray Tomography (CT) Facility at DLR



X-Ray CT Facility v|tome|x L450 at DLR Stuttgart

3 dimensional non intrusive  
imaging of SOFC cassette



Deutsches Zentrum  
für Luft- und Raumfahrt e.V.  
in der Helmholtz-Gemeinschaft



## Summary

- The measuring techniques and exemplary results proved the possibility of
  - identifying different degradation mechanisms in fuel cells
  - optimizing operating conditions in fuel cells
  - establishing control strategies for reliable operation of fuel cells
  
- Combined in-situ and ex-situ diagnostic methods can provide additional important information:
  - Spatially resolved measurements to obtain local distribution of cell properties (current, voltage, impedance, gas composition, temperature)
  - Application of combined in-situ and ex-situ analytical methods
  - Combined analytical and modeling approach
  
- In order to overcome the remaining challenges in fuel cell development, i.e. performance, durability, reliability and costs, it is of paramount importance to improve the understanding of fuel cell operating mechanisms by applying sophisticated analytical methodology